# Relative Permeabilities of Plastic Films to Water and Carbon Dioxide

### Joseph T. Woolley

Soil and Water Conservation Research Division, Agricultural Research Service, United States Department of Agriculture, and Department of Agronomy, University of Illinois, Urbana, Illinois 61801

Received January 19, 1967.

Summary. The permeabilities of several types of plastic films to water and to carbon dioxide were measured. No material was found to have a carbon dioxide permeability as great as its water permeability.

One possible way in which we might reduce transpiration is by applying a coating over the leaf, including the stomatal apertures. Such a coating would have to be more permeable to CO<sub>2</sub> than to water, so we would first like to know what materials have this property. Statements in the literature that polyethylene has a high permeability to CO<sub>2</sub> and a low permeability to water vapor (8, p 267) give the impression (4) that polyethylene is more permeable to CO2 than to water vapor. Such statements are misleading because they refer to polyethylene in comparison to other common packaging films. Published data (1, 2, 3, 5, 7, 8, 9, 10, 11) indicate that polyethylene does have a lower permeability to water vapor than do many films, and a higher permeability to CO2 than do many films, but that polyethylene is more permeable to water vapor than to CO2. Unfortunately, the permeability data for any given material are extremely variable, many different units have been used, and few workers have measured both H2O and CO2 permeabilities of a given film. Adding to the confusion are the numerous errors in published tabulations of film properties (6). To overcome the uncertainties of this situation, I measured CO2 and water permeabilities on the same pieces of several different films, using similar methods and apparatus for both measurements. The techniques were designed to give the best comparison of the 2 permeabilities for a given film, rather than to give accurate absolute values for these permeabilities.

# Methods

One unit of the apparatus is shown schematically as figure 1. A sheet of film 12.0 cm in diameter

was clamped by a rubber gasket around its edge in the transparent acrylic apparatus so that a circle of film 10.2 cm in diameter was exposed for passage of water vapor or CO2. Water-saturated air or dried CO<sub>2</sub> was passed through the apparatus across the top of the film and thence through polyethylene tubing (2 mm inside diameter, 30 cm long) to the external atmosphere. The absorbent below the film was weighed periodically to give the weight of gas or vapor which had passed through the film. The absorbent was activated alumina for water vapor measurement and was NaOH on asbestos granules (Ascarite, Arthur H. Thomas Co., Philadelphia)1 and activated alumina for CO<sub>2</sub> measurements. The plastic dish holding the absorbent could be removed and weighed while the film under test remained mounted. To prevent pressure differentials from developing across the film, access to the atmosphere from the absorbent chamber was allowed through a small polyethylene tube and 2 beds of absorbent. These latter 2 beds were changed at the beginning of each run, but were usually weighed only during the initial development and testing of the apparatus, to give an indication of how much gas or vapor

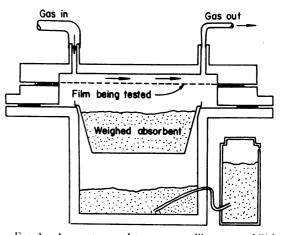


Fig. 1. Apparatus used to measure film permeabilities.

<sup>&</sup>lt;sup>1</sup> Trade names and company names are included for the benefit of the reader and do not imply any endorsement or preferential treatment of the named product by the United States Department of Agriculture or the University of Illinois.

might be entering through this path. For each run, 4 units of the apparatus were used with saturated air and 4 with CO<sub>2</sub>. Of these 4, 2 had 1 layer of film, while the other 2 had 2 layers mounted together.

The data for an entire run of 8 units were rejected unless they met the following criteria: A) The total weight gain for either gas with 1 layer of film was between 1.80 and 2.05 times the weight gain with 2 layers of film. B) The weight gains of duplicate units did not differ by more than 10 % of their average value. Thus I single aberrant value would cause the rejection of the data from all 8 units used in that run. With these criteria, the data from about one-fourth of the runs were rejected. At the end of a successful run, another run was made with the same films, but with the water vapor and carbon dioxide units interchanged. Thus each individual piece of film was tested with both water vapor and CO2. The actual datum used in each calculation of permeability was neither that from the single films nor that from the double films, but was the weight gain of the 2 single film units minus the weight gain of the 2 double film units. This seemed to be the best way to correct for small leaks or for water or CO2 absorbed during opening and closing of the apparatus.

It is evident from this description that the water and CO<sub>2</sub> permeabilities were run under similar, but not exactly the same conditions. The CO<sub>2</sub> measurements were made with a CO<sub>2</sub> partial pressure differential of about 75 cm Hg, at essentially zero relative humidity. The water permeability measurements had a water partial pressure differential of about 1.86 cm Hg (at 21°), with 100 % relative humidity on 1 side of the film, zero relative humidity humidity

midity on the other. In contrast, the water partial pressure differential between a leaf and the ambient air is much greater than the CO<sub>2</sub> partial pressure differential between the same 2 locations. Further, with a leaf, both CO<sub>2</sub> and H<sub>2</sub>O move simultaneously but in opposite directions. No allowances were made for these differences and no attempt was made to simulate the actual leaf situation.

## Results

The permeabilities found are given in table 1, in units of mm<sup>4</sup>sec<sup>-1</sup>dvne<sup>-1</sup>. Each mm<sup>4</sup>sec<sup>-1</sup>dvne<sup>-1</sup> is equivalent to 10<sup>-10</sup> cm<sup>3</sup> of gas or water vapor at standard temperature and pressure passing through 1 cm2 of film 1 cm thick each second with a partial pressure differential of 1 bar. Table I also gives an arbitrarily defined figure of merit for each material, this figure of merit being 1.6 times the ratio of the CO<sub>2</sub> permeability to the H<sub>2</sub>O permeability. The figure of merit is used because the diffusion coefficient of water vapor in air is about 1.6 times as great as the diffusion coefficient of CO<sub>2</sub> in air, so that with a given gradient, 1.6 times as much water as CO<sub>2</sub> would diffuse through an open hole, such as a stomate. A figure of merit greater than unity would indicate a film which was more effective than an open hole in limiting water vapor movement without limiting carbon dioxide movement.

None of the films had a higher permeability to carbon dioxide than to water, and no figure of merit for film was greater than 1, so none of the materials tested would be of more use to the plant than would the stomates in controlling transpiration without interfering with carbon dioxide movement. Actually, a small hole in aluminum foil

| Table I. Permeabilities of Films to Carbon Dioxide and I | Water | r |
|----------------------------------------------------------|-------|---|
|----------------------------------------------------------|-------|---|

| Film material                                         | Trade name    | Manufacturer         | Approximate thickness, microns | Permeability |                               |                  |
|-------------------------------------------------------|---------------|----------------------|--------------------------------|--------------|-------------------------------|------------------|
|                                                       |               |                      |                                | $CO_2$       | $ m H_2O$ $ m ^{-1}dyne^{-1}$ | Figure of merit* |
| Fluorinated ethylene propylene                        | Teflon        | E. I. duPont         | 13                             | 830          | 1600                          | 0.82             |
| Polyethylene                                          |               |                      | 25                             | 760          | 6800                          | 0.18             |
| Rubber dental dam                                     |               |                      | 200                            | 11,000       | 130.000                       | 0.14             |
| Paraffine and rubber?                                 | Parafilm      | American Can Co.     | 130                            | 4000         | 69,000                        | 0.093            |
| Oriented styrene                                      |               |                      | 76                             | 700          | 88,000                        | 0.013            |
| Polycarbonate                                         | Lexan         | General Electric Co. | 130                            | 1300         | 210,000                       | 0.0096           |
| Polyvinylidene chloride polyvinyl chloride copolymer? | Saran-wrap    | Dow Chemical Co.     | 13                             | 4.1          | 910                           | 0.0071           |
| Cellulose acetate                                     |               |                      | 190                            | 1900         | 610.000                       | 0.0050           |
| Regenerated cellulose                                 | Cellophane    |                      | 25                             | 9500         | 3.300.000                     |                  |
| Polyethylene glycol<br>terephthalate (polyester)      | Mylar         | E. I. duPont         | 13                             | 12           | 8600                          |                  |
| Hole about 0.01 cm in diameter                        | r in aluminum | foil sheet           |                                |              |                               | 1.3**            |

<sup>\*</sup> Figure of merit for films is  $\frac{\text{CO}_2 \text{ permeability} \times 1.6}{\text{H}_2\text{O} \text{ permeability}}$ 

observed  $CO_2$  diffusion coefficient  $\times$  1.6

observed H.,O diffusion coefficient

<sup>\*\*</sup> Figure of merit for hole in aluminum foil is

gave a figure of merit of 1.3, rather than the expected 1.0. This was probably because the smallest easily reproducible hole offered comparatively little resistance to water or CO<sub>2</sub> diffusion. Thus other factors than the presence of the intended barrier could have limited the movement.

#### Discussion

These permeabilities do not differ greatly from those available in the literature for some of these materials, and I can find no data in the original literature that would indicate that any material in existence has a higher permeability to carbon dioxide than to water vapor (1, 2, 3, 5, 7, 10). Two classes of materials which I have not yet been able to test successfully are very thin metals and plant leaf waxes, such as carnauba wax. Carnauba wax is too brittle to be tested as described here, but I hope to be able to coat a very thin layer of the wax on a polyethylene film and to test the combination. The same technique should succeed for metals, because several films with very thin metal coatings are commercially available.

The permeabilities of some films, such as the cellulosics, depend fairly strongly on the thickness of the film under test (3,7). Only 1 thickness of each film was tested completely, but the cellulosics had very low figures of merit.

Even if a material having the desired permeability characteristics is found, we will still be faced with all of the practical difficulties mentioned by Gale and Hagan (4) and by Waggoner (11), but the potential gains to be derived would justify a large amount of technological research. It appears, however, that a material with the desired qualities may not exist.

# Acknowledgments

I thank Miss Heidi Stahnke for valuable and dependable assistance.

#### Literature Cited

- BRUBAKER, D. W. AND K. KAMMERMEYER. 1952. Separation of gases by means of permeable membranes. Ind. Eng. Chem. 44: 1465-74.
- Brubaker, D. W. and K. Kammermeyer. 1953. Flow of gases through plastic membranes. Ind. Eng. Chem. 45: 1148-52.
- Brubaker, D. W. and K. Kammermeyer. 1954. Separation of gases by plastic membranes. Ind. Eng. Chem. 46: 733–39.
- GALE, J. AND ROBERT M. HAGAN. 1966. Plant antitranspirants. Ann. Rev. Plant Physiol. 17: 269–82.
- JESCHKE, D. AND H. A. STUART. 1961. Diffusion und Permeation von Gasen in Hochpolymeren in Abhängigkeit von Kristallisationsgrad und von der Temperatur. Z. Naturforsch. 16a: 37–50.
- Modern Plastics Encyclopedia for 1967. 1966. Modern Plastics 44 (No. 1A). McGraw Hill Inc. New York.
- Morgan, P. W. 1953. Structure and moisture permeability of film forming polymers. Ind. Eng. Chem. 45: 2296–306.
- 8. RAFF, R. A. V. AND J. B. ALLISON. 1956. Polyethylene. High Polymers Vol. XI. Interscience Publishers Inc. New York, 551 p.
- STANNETT, V. AND H. YASUDA. 1964. Permeability
  In: Crystalline Olefin Polymers. High Polymers
  Vol. XX. R. A. V. Raff and K. W. Doak, eds.
  John Wiley and Sons Inc. New York, p 131–84.
- VAN AMEROGEN, G. J. 1949. Influence of structures of elastomers on their permeability to gases. J. Polymer Sci. 5: 307-32.
- WAGGONER, PAUL E. 1966. Decreasing transpiration and the effect upon growth. In: Plant Environment and Efficient Water Use, W. H. Pierre et al., eds. American Society of Agronomy. Madison, Wisconsin. p 49-72.